

PCT

WORLD INTELLECTUAL PROPERTY  
ORGANIZATION



INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9606875A1

(51) International Patent Classification <sup>6</sup> : <b>C08G 18/48, 18/66</b>	<b>A1</b>	(11) International Publication Number: <b>WO 96/06875</b>
		(43) International Publication Date: 7 March 1996 (07.03.96)

(21) International Application Number: PCT/US94/12469  
(22) International Filing Date: 1 November 1994 (01.11.94)  
(30) Priority Data:  
08/299,394 1 September 1994 (01.09.94) US  
(71) Applicant: W.L. GORE & ASSOCIATES, INC. [US/US]; 551  
Paper Mill Road, P.O. Box 9206, Newark, DE 19714 (US).  
(72) Inventors: DELANEY, Pamela, J.; 4 McCormick Drive,  
Hockessin, DE 19707 (US). LEONE, Shaun; 216 W.  
Edgewater Way, Newark, DE 19713 (US).  
(74) Agents: SAMUELS, Gary, A. et al.; W. L. Gore & Associates,  
Inc., 551 Paper Mill Road, P.O. Box 9206, Newark, DE  
19714 (US).

(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN,  
CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU,  
LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD,  
SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE,  
DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

**Published**  
*With international search report.*

(54) Title: HYDROPHILIC POLYURETHANE

(57) Abstract

The invention is achieved by a polyurethane that is the reaction product of 4,4'-diphenylmethane diisocyanate (MDI), poly(oxyethylene)glycol (PEG), and 1,4-butane diol (BDO). The equivalents of each reactant in the polyurethane is 4:1:3. Polyethylene glycol 1450 is preferred. The amount of hard segment (made up of chain extender and MDI) is about 46 weight percent. The polymer is unusually tough and has good tensile strength and wet strength.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

**TITLE OF THE INVENTION****HYDROPHILIC POLYURETHANE**

5

**FIELD OF THE INVENTION**

This invention relates to a breathable, elastomeric, thermoplastic liquid-waterproof polyurethane of very good toughness and tensile strength.

10

**BACKGROUND OF THE INVENTION**

Polyurethanes are prepared from an isocyanate, a polyol and a chain extender. Depending on the equivalency ratios of the reactants, the processing techniques and the properties can be varied.

15

Thermoplastic polyurethanes are of two types. One type is prepared by the reaction of essentially equivalents of isocyanate and active hydrogen functionality, so that little crosslinking occurs after formation of the polymer. The other type is slightly crosslinkable due to an excess of isocyanate groups. This invention is concerned with the former.

20

Historically, it has been difficult to obtain desirable physical characteristics such as tensile strength, elongation, tear strength, toughness and the like in highly hydrophilic polymeric coatings, especially if the polymer swells in solvents.

25

U.S. Patent 4,273,911 discloses low melt temperature processible thermoplastic polyurethanes prepared by employing two melt point lowering diol chain extenders and a strength enhancing diol.

Breathable polyurethanes, i.e., ones that have the ability to transport water molecules through them are made using a polyol of polyoxyethylene, such as are disclosed in U.S. Patent 3,164,565, and U.S.P. 3,901,852.

30

U.S. Patent 4,367,327 discloses a film of polyoxyethylene polyurethane which provides breathability, but a compromise is made for breathability and elastomeric properties.

35

U.S. Patent 4,532,316 teaches reactive, segmented polyurethane prepolymers that can be breathable, especially when employing a polyol of polyoxyethylene. The prepolymer is melt-processible at low temperatures and has good water vapor transmission rates. In these polymers the chain extender is present in less ratios than the other ingredients.

-2-

It is an object of this invention to achieve even better polyurethanes in terms of strength including wet strength, and in terms of breathability, and low swell properties.

5

### SUMMARY OF THE INVENTION

The invention is achieved by a polyurethane that is the reaction product of 4,4'-diphenylmethane diisocyanate (MDI), poly(oxyethylene) glycol (PEG), and 1,4-butane diol (BDO). The equivalents of each reactant in the polyurethane is 4:1:3. Polyethylene glycol 1450 is preferred. The amount of hard segment (made up of chain extender and MDI) is about 46 weight percent.

This polymer is unexpectedly strong, especially with regard to toughness (wet or dry), and tensile strength. The polymer is breathable, elastomeric, and has good hand and low swell. It is useful as a fabric coating in imparting durability to fabrics while maintaining good breathability. It is also useful as a water vapor permeable adhesive, or a permeable membrane, or the like.

By "breathable" is meant that the polymer transports water vapor molecules through the polymer.

By "elastomeric" is meant that the polymer film can be stretched and upon release of the stretching force retracts to approximately its original shape.

### BRIEF DESCRIPTION OF THE DRAWINGS

25

Figure 1 is a graph comparing the toughness of the Example 1 sample of the invention with comparisons described below.

Figures 2 and 3 are bar charts comparing wet and dry tensile strength values (Figure 2) and toughness values (Figure 3) of the Example 1 sample with the comparisons.

30

### DETAILED DESCRIPTION OF THE INVENTION

It has unexpectedly been discovered that when MDI/PEG/BDO is employed in the polyurethane in a 4:1:3 ratio and the hard segments comprise about 46 weight percent of the polyurethane, the polymer has an unusually high tensile strength, toughness, and low swell while maintaining high moisture vapor permeability, and has good wet strength properties. A polymer fulfilling

35

-3-

this description is a 4:1:3 equivalent ratio made of MDI/PEG 1450/BDO having a percentage of hard segments of 46 weight percent.

It is well known that polyurethanes have hard and soft segments. The hard segments are made up of units of MDI and BDO. The soft segments are the PEG units. Degree of breathability is controlled by the amount of PEG present in the polymer, and increases as the amount of PEG increases. PEG also imparts resistance to hydrolysis and fungus, and imparts good flexibility at low temperature. The BDO is a chain extender (CE) which increases the chain length and molecular weight of the polymer.

The polymer can be synthesized by conventional procedures. Two convenient procedures are the "prepolymer" method and the "one-step" method. In the former MDI is ordinarily preheated to 50 - 70°C, preferably 50°C, and then polyethylene glycol (PEG) 1450 (that has been degassed) added at a 4:1 MDI/PEG ratio. The reactor is sealed under an inert atmosphere such as nitrogen, and the mixture stirred for a time and temperature to permit reaction of the MDI and PEG. Then the chain extender is rapidly added at 50-90°C in an amount to make the 4:1:3 ratio. Stirring was continued until the mixture begins to thicken. It is poured in a container, sealed under nitrogen and stored.

In the "one-step" procedure, the PEG and the BDO can be weighed in a reaction vessel at a ratio of 1:3 and stirred. 4 parts of MDI can then be rapidly added and the vessel contents stirred. The reaction mass will thicken and heat will evolve. The container mixture can then be closed under nitrogen, sealed and the mixture stored.

It may be desirable, but not essential, to include a catalyst in the reaction mixture employed to prepare the prepolymers of this invention. Any of the catalysts conventionally employed in the art to catalyze the reaction of an isocyanate with a compound containing an active hydrogen can be employed for this purpose. The amount of catalyst employed is generally within the range of about 0.02 to about 2.0 percent by weight of the reactants.

The polymers can be comminuted into a more workable form. To make films, the polymer can be dissolved in a solvent, such as N-methyl-2-pyrrolidinone (NMP), N,N-dimethyl formamide, tetrahydrofuran (THF), phenol, or dimethyl sulfoxide, and then cast onto a flat substrate. Alternatively, the polymer, being thermoplastic, can simply be extruded into a desired form.

The polymer can also be coated or laminated onto a substrate from solution or can be extrusion coated onto the substrate. Being thermoplastic, the polymers can be extruded without having to use a solvent. Substrates that

-4-

can be coated include fabrics, and porous or nonporous films or membranes, such as textiles, polymeric membranes, papers, padding and the like. One such membrane is stretched porous polytetrafluoroethylene which has a microstructure of nodes interconnected with fibrils.

5       The polymers can also be applied as an adhesive to bind together two substrates described above.

      If desired, the polymers of this invention can have incorporated in them, at any appropriate stage of preparation, additives such as pigments, fillers, lubricants, stabilizers, antioxidants, coloring agents, fire retardants and the like, which are commonly used in conjunction with polyurethane elastomers. 10       The same care must be taken to ensure low moisture levels of the additives as appropriate in conventional polyurethane prepolymer technology.

#### WATER VAPOR TRANSMISSION RATE (MVTR)

15

      In the procedure, approximately 70 ml. of a solution consisting of 35 parts by weight of potassium acetate and 15 parts by weight of distilled water was placed into a 133 ml. polypropylene cup, having an inside diameter of 6.5 cm. at its mouth. A PTFE membrane having a MVTR of approximately 34,200 20 g/[M<sup>2</sup> x 24 hr.] as tested by the method described in U.S. Patent 4,862,730 to Crosby and available from W. L. Gore & Associates, Inc. of Newark, Delaware, was heat sealed to the lip of the cup to create a taut, leakproof, microporous barrier containing the solution.

      A similar expanded PTFE membrane was mounted to the surface of a 25 water bath. The water bath assembly was controlled at 23°C plus or minus 0.2°C, utilizing a temperature controlled room and a water circulating bath.

      The sample to be tested was allowed to condition at a temperature of 23°C and a relative humidity of 50% prior to performing the test procedure. Samples were placed so the sample was in contact with the expanded 30 polytetrafluoroethylene membrane mounted to the surface of the water bath and allowed to equilibrate 30 minutes prior to the introduction of the cup assembly.

      The cup assembly was weighed to the nearest 1/1000g. and was placed in an inverted manner onto the center of the test sample.

35       Water transport was provided by the driving force between the water in the water bath and the saturated salt solution providing water flux by diffusion in that direction. The sample was tested for 15 minutes and the cup assembly was then removed, weighed again within 1/1000g.

The MVTR of the sample was calculated from the weight gain of the cup assembly and was expressed in grams of water per square meter of sample surface area per 24 hours.

5

### TENSILE PROPERTIES

Tensile tests were performed according to ASTM D882-88, Method A, with the following two exceptions:

1. the distance between the grips as was stated in Section 10.3 was changed to 1 inch; and
2. the crosshead speed was 10 inches/minute.

The values specified in Table 2 of the ASTM were not used. The Instron testing machine used was Model 1122, equipped with a strip chart recorder. All samples were tested using a 50 lb. load cell.

15

The scope of this method states that this method covers the determination of tensile properties of plastics in the form of thin sheeting, including film less than 0.04 inches in thickness. Method A is the Static Weighing -Constant-Rate-Of-Grip Separation Test, which employs a constant rate of separation of the grips holding the ends of the test specimen.

20

Toughness refers to the Tensile Energy to Break (TEB) as defined in Section 3.4 of this method. Toughness is used to evaluate materials that may be subjected to heavy abuse.

Test specimens were cut using a razor in accordance with Section 5 and other considerations set forth in Section 6. Conditioning was done as explained in Section 7, with the exception of the wet specimen testing. Wet tensile tests were performed using ASTM D882-88 Method A (with exceptions as noted above) on samples that had been conditioned in distilled water for 24 hours at ambient temperature.

25

All calculations for both the wet and dry specimens were done in compliance with Section 11 and Annex A1.

30

EXAMPLESRaw Materials Used

5           "Carbowax" brand "Sentry" polyethylene glycol 1450, "Carbowax" brand "Sentry" polyethylene glycol 1000, and "Carbowax" brand "Sentry" polyethylene glycol 3350, were all obtained from Union Carbide Corporation.

          4,4' diphenylmethane diisocyanate was obtained from ICI Polyurethanes as Rubinate 44.

10           1,4-Butanediol was obtained from DuPont Chemicals.

          Hard segment content of the polymers is weight percent.

Example 1

15           Preparation of MDI/PEG 1450/BDO, 4:1:3 at 46% hard segment

Prepolymer technique

          A polymer of this invention was prepared from 144.9 grams (4 equivalents) of 4,4'-diphenylmethane diisocyanate, 215.8 grams (1 equivalent) polyethylene glycol having a molecular weight of 1450 and 39.2 grams (3 equivalents) of 1,4-butanediol.

          In preparation for this reaction the polyethylene glycol was degassed under vacuum for 2 hours at 100°C. It was blanketed with nitrogen then stored at 75°C until ready to use. The 4,4'-diphenylmethane diisocyanate was blanketed with nitrogen and stored at 40°C until melted and ready to use. A 1 liter jacketed reactor was purged with nitrogen and preheated to 50°C. The 4,4'-diphenylmethane diisocyanate was charged into the reactor and stirred. The polyethylene glycol was then also charged into the reactor with stirring and the temperature of the reactor was increased to 85°C. It was stirred for 2 hours under nitrogen. At the end of 2 hours the 1,4-butanediol was added all at once. The mixture was stirred vigorously for several minutes after which time the mixture began to thicken and the color turned from clear to white. The polymer, which was still pliable, was transferred to a metal container, blanketed with nitrogen and sealed.

35           Films were prepared by sheet extrusion or solution casting, and tested. Property values are set forth in Tables 1 and 2. MVTR of a 1.5 mil film was 9,000.



**Comparison Example A****Preparation of MDI/PEG 1450/BDO, 4:2:2 at 28% hard segment**

5           The reaction materials were prepared as described above. A metal  
container was selected as the reaction vessel and 286.48 grams (2  
equivalents) of the liquid polyethylene glycol was weighed into the container  
followed by the addition of 17.32 grams (2 equivalents) 1,4-butanediol. The  
mixture was swirled to mix. 96.2 grams (4 equivalents) of the liquid 4,4'-  
10   diphenylmethane diisocyanate was quickly added. The container was held  
under an overhead stirrer and heated briefly with a heatgun. The mixture  
became very hot. It was blanketed with nitrogen and sealed. Films were cast  
using NMP or THF, but were sticky and unsuitable for measurement of tensile  
properties by the procedure described above. MVTR for a 1 mil film was  
15   15,217.

**Comparison Example B****Preparation of MDI/PEG 3350/BDO, 4:1:3 at 26% hard segment**

20           The reaction materials were prepared as described above. A metal  
container was again selected as the reaction vessel and 239.3 grams (1  
equivalent) of the liquid polyethylene glycol was weighed into the container,  
followed by the addition of 22.7 grams (3 equivalents) of the liquid 1,4-  
25   butanediol. The container was warmed with a heatgun and swirled to mix.  
84.4 grams (4 equivalents) of 4,4'-diphenylmethane diisocyanate was added  
rapidly and the container was held under a mechanical stirrer. The mixture  
quickly became very hot. It was blanketed with nitrogen and the container was  
sealed.

30           Films were made as described in Comparison A. Test results are set  
forth in Tables 1 and 2. MVTR for a 1 mil film was 25,238.

**Comparison Example C****Preparation of MDI/PEG 1000/BDO, 4:1:3 at 55% hard segment**

Th reactants were prepared as described above. The reactor was  
purged with nitrogen and preheated to 50°C. A prepolymer was prepared by

charging 176 grams (4 equivalents) of 4,4'-diphenylmethane diisocyanate into the reactor and then charging 177 grams (1 equivalent) of the liquid polyethylene glycol into the reactor with stirring. The reactor temperature was increased to 85°C and it was stirred for 2 hours under nitrogen. After 2 hours had elapsed, 47.5 grams (3 equivalents) 1,4-butanediol were quickly added. It was stirred vigorously and began to turn white and solidify quickly. It was transferred from the reactor to a metal container with some difficulty. The mixture was blanketed with nitrogen and sealed.

Films were made as described in Comparison A and test results are set forth in Tables 1 and 2. MVTR for a 3.8 mil film was 3428.

#### Comparison Example D

##### Preparation of 4:1.5:2.5, MDI/PEG 1000/BDO, 45% hard segment

##### One Shot method

The reaction materials were prepared as previously described. A metal can was again selected as the reaction vessel and 220.8 grams (1.5 equivalents) of the liquid polyethylene glycol was weighed into the can, followed by the addition of 32.8 grams (2.5 equivalents) of the liquid 1,4-butanediol. The can was warmed with a heatgun and swirled to mix. 146 grams (4 equivalents) of 4,4'-diphenylmethane diisocyanate was added rapidly and the can was held under a mechanical stirrer. The mixture quickly became very hot. It was blanketed with nitrogen and the can was sealed. Films were made as in Comparison A and tested. MVTR for a 0.8 mil film was 12,600.

#### Comparison Example E

##### Preparation of 4:1.5:2.5, MDI/PEG 1450/BDO, 36% hard segment

##### One-shot method

The reaction materials were prepared as previously described. A metal can was again selected as the reaction vessel and 258.4 grams (1.5 equivalents) of the liquid polyethylene glycol was weighed into the can, followed by the addition of 26.0 grams (2.5 equivalents) of the liquid 1,4-butanediol. The can was warmed with a heatgun and swirled to mix. 115.6

-9-

grams (4 equivalents) of 4,4'-diphenylmethane diisocyanate was added rapidly and the can was held under a mechanical stirrer. The mixture quickly became very hot. It was blanketed with nitrogen and the can was sealed. Films were made as described in Comparison A and tested. MVTR for a 2 mil film was 11,800.

#### Comparison Example F

##### Preparation of 4:0.75:3.25, MDI/PEG 1450/BDO, 54% hard segment

##### One-shot method

The reaction materials were prepared as previously described. A metal can was again selected as the reaction vessel and 169 grams (0.75 equivalents) of the liquid polyethylene glycol was weighed into the can, followed by the addition of 43.8 grams (3.25 equivalents) of the liquid 1,4-butanediol. The can was warmed with a heatgun and swirled to mix. 151 grams (4 equivalents) of 4,4'-diphenylmethane diisocyanate was added rapidly and the can was held under a mechanical stirrer. The mixture quickly became very hot. It was blanketed with nitrogen and the can was sealed. Films were made as described in Comparison A and tested. MVTR for a 1 mil film was 6660.

**TABLE 1 - TEST DATA ON TENSILE PROPERTIES****Example 1**

- 5      **Formulation: 4:1:3, MDI: PEG 1450: BDO - 46% Hard Segment**  
**Solution cast film**

	DRY	WET
Tensile Strength	7,151 psi	3,764 psi
Elongation	580%	539%
Toughness	14,550 in. per lb./in. <sup>3</sup>	8,678 in. per lb./in. <sup>3</sup>

**Extruded batch of film - ANNEALED\***

	DRY	WET
Tensile Strength	12,360 psi	6,471 psi
Elongation	630%	493%
Toughness	33,160 in. per lb./in. <sup>3</sup>	16,180 in. per lb./in. <sup>3</sup>

\*annealed for 2.5 hrs. @ 100°C, then 3 hrs. @ 320°C, then 17 hrs @ 90°C

10

**Extruded batch of film - NOT ANNEALED**

	DRY	WET
Tensile Strength	12,360 psi	4,293 psi
Elongation	502%	540%
Toughness	24,640 in. per lb./in. <sup>3</sup>	12,590 in. per lb./in. <sup>3</sup>

**Comparison Example A**

**Formulation: 4:2:2, MDI: PEG 1450: BDO - 28% Hard Segment**

15

Data unavailable, film was too sticky to remove from release surface and cut into ASTM specimens for testing.

**Comparison Example B**

20      **Formulation: 4:1:3, MDI: PEG 3350: BDO - 26% Hard Segment**

	DRY	WET
Tensile Strength	2,400 psi	257 psi
Elongation	10.9%	122.7%
Toughness	125 in. per lb./in. <sup>3</sup>	171 in. per lb./in. <sup>3</sup>

**Comparison Example C****Formulation: 4:1:3, MDI: PEG 1000: BDO - 55% Hard Segment**

	DRY	WET
Tensile Strength	2,010 psi	1,551 psi
Elongation	301.2%	139.9%
Toughness	4,697 in. per lb./in. <sup>3</sup>	1,640 in. per lb./in. <sup>3</sup>

**Comparison Example D****5 Formulation: 4:1.5:2.5, MDI: PEG 1000: BDO - 45% Hard Segment**

	DRY	WET
Tensile Strength	1,592 psi	1,480 psi
Elongation	535%	380%
Toughness	5,186 in. per lb./in. <sup>3</sup>	4,919 in. per lb./in. <sup>3</sup>

**Comparison Example E****Formulation: 4:1.5:2.5, MDI: PEG 1450: BDO - 36% Hard Segment**

	DRY	WET
Tensile Strength	180 psi	343 psi
Elongation	53%	95%
Toughness	140 in. per lb./in. <sup>3</sup>	1,178 in. per lb./in. <sup>3</sup>

**Comparison Example F****10 Formulation: 4:0.75:3.25, MDI: PEG 1450: BDO - 54% Hard Segment**

	DRY	WET
Tensile Strength	2,200 psi	1,814 psi
Elongation	380	280%
Toughness	5,300 in. per lb./in. <sup>3</sup>	4,500 in. per lb./in. <sup>3</sup>

15 In Figures 1-3, the comparison data is plotted with Example 1 data to graphically show the differences. In Figure 1, the values for toughness versus percent hard segment is compared. The data shows the unexpected degree of toughness of 14,550 inch/lb./inch<sup>3</sup> for the Example 1 polymer.

20 In Figure 2, a bar chart is shown which depicts the tensile strength values, dry and wet, for the Example 1 and the comparisons. In Figure 3, toughness values are depicted. In Figures 2 and 3 the dry strength is the first bar and wet strength is the adjacent bar to the immediate right. It is seen in the two charts that the Example 1 values for both dry and wet determinations

are superior to the values of the comparisons. It is also seen that the Example 1 sample is stronger and tougher wet than are the comparison samples dry.

#### TABLE 2 - TEST DATA ON SWELL

5

##### Low Swell

The formulation of Example 1 has unexpectedly low swelling properties for a hydrophilic polyurethane. Swell was measured by using a 1 inch circular die to stamp out discs of film. The discs were then allowed to sit in a vacuum oven at ambient temperature to remove any moisture that may have been absorbed. The discs were then soaked in distilled water for 24 hours and then measured for size increase.

15 Example 1 - swell ranged from 7-18% (several samples)

Comparison Example A - 37.5%

Comparison Example B - 50%

Comparison Example C - 8.3%

20 Comparison Example D - 6.25%

Comparison Example E - 25%

Comparison Example F - 6.25%

It is seen that Example 1 has the unique combination of properties:

25

- low swell
- excellent retention of tensile properties when wet
- excellent breathability
- high strength

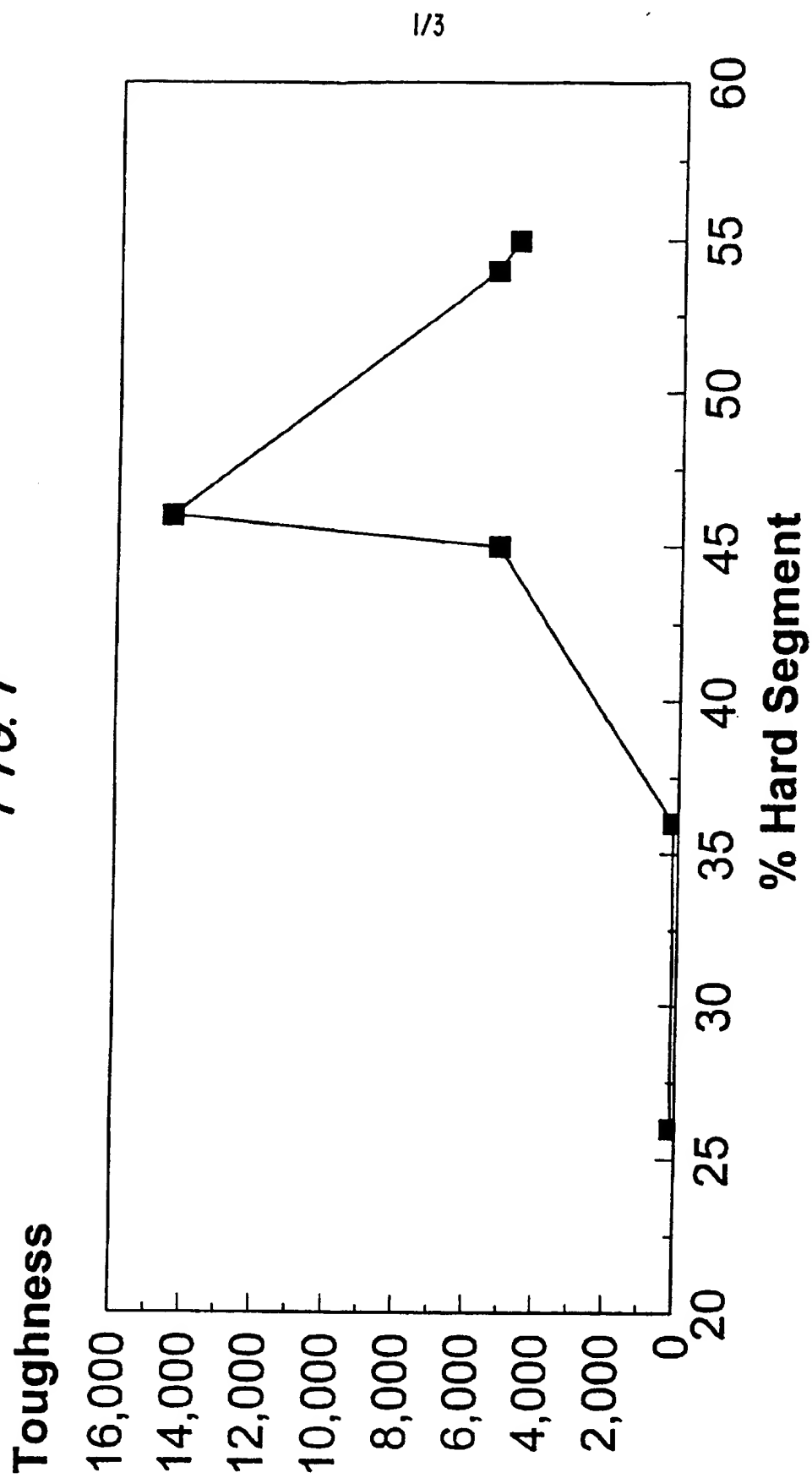
30

**CLAIMS:**

1. A polyurethane comprising the reaction product of:
  - (a) 4,4'-diphenylmethane diisocyanate;
  - 5 (b) polyoxyethylene glycol; and
  - (c) 1,4-butanediol

in which the equivalents of each reactant a), b) and c) in the reaction mixture are in the ratio 4:1:3, and the amount of a) and c) present in about 46 weight percent of the total weight of the polyurethane.
- 10 2. The polyurethane of Claim 1 wherein the polyoxyethylene glycol is polyoxyethylene glycol 1450.

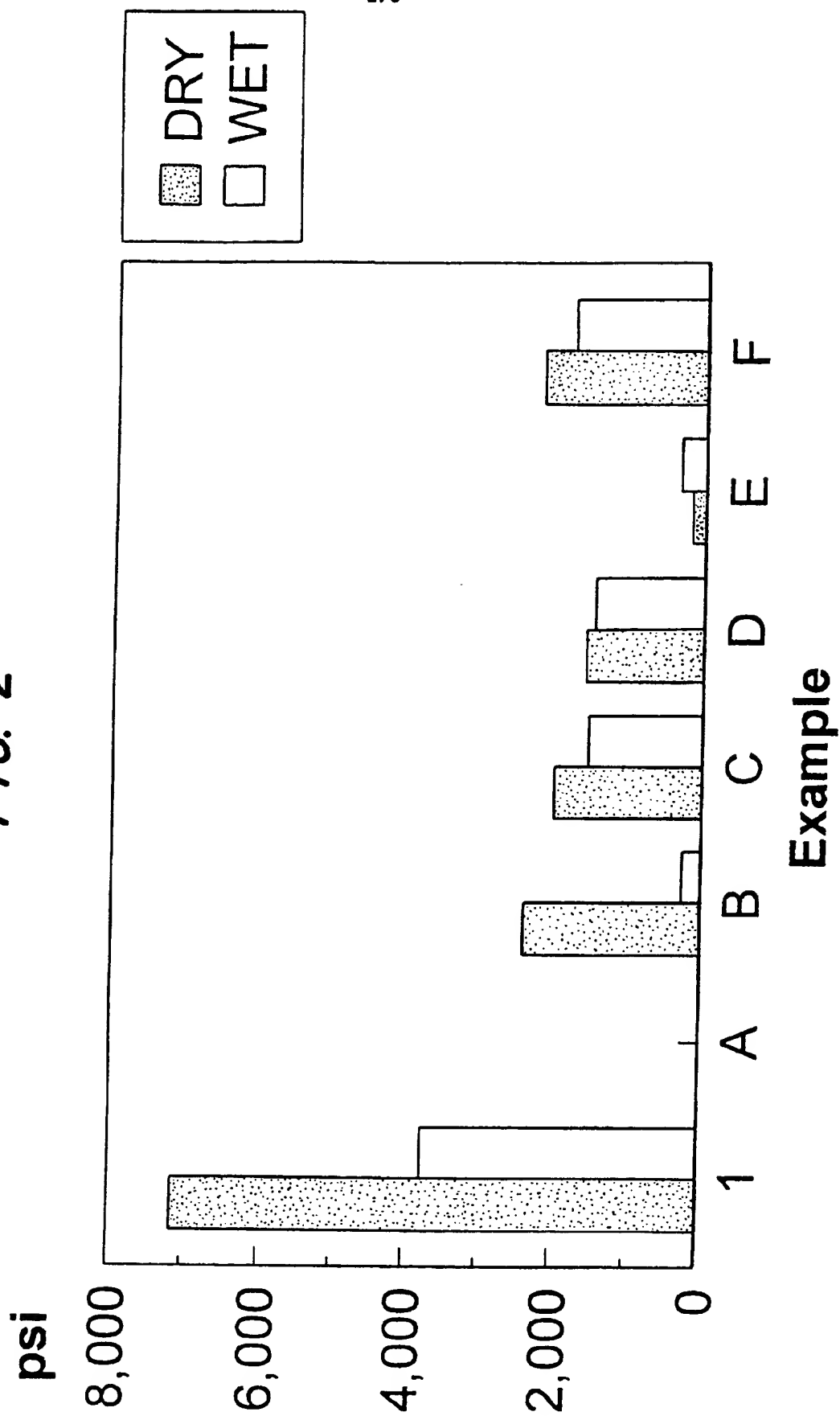
FIG. 1





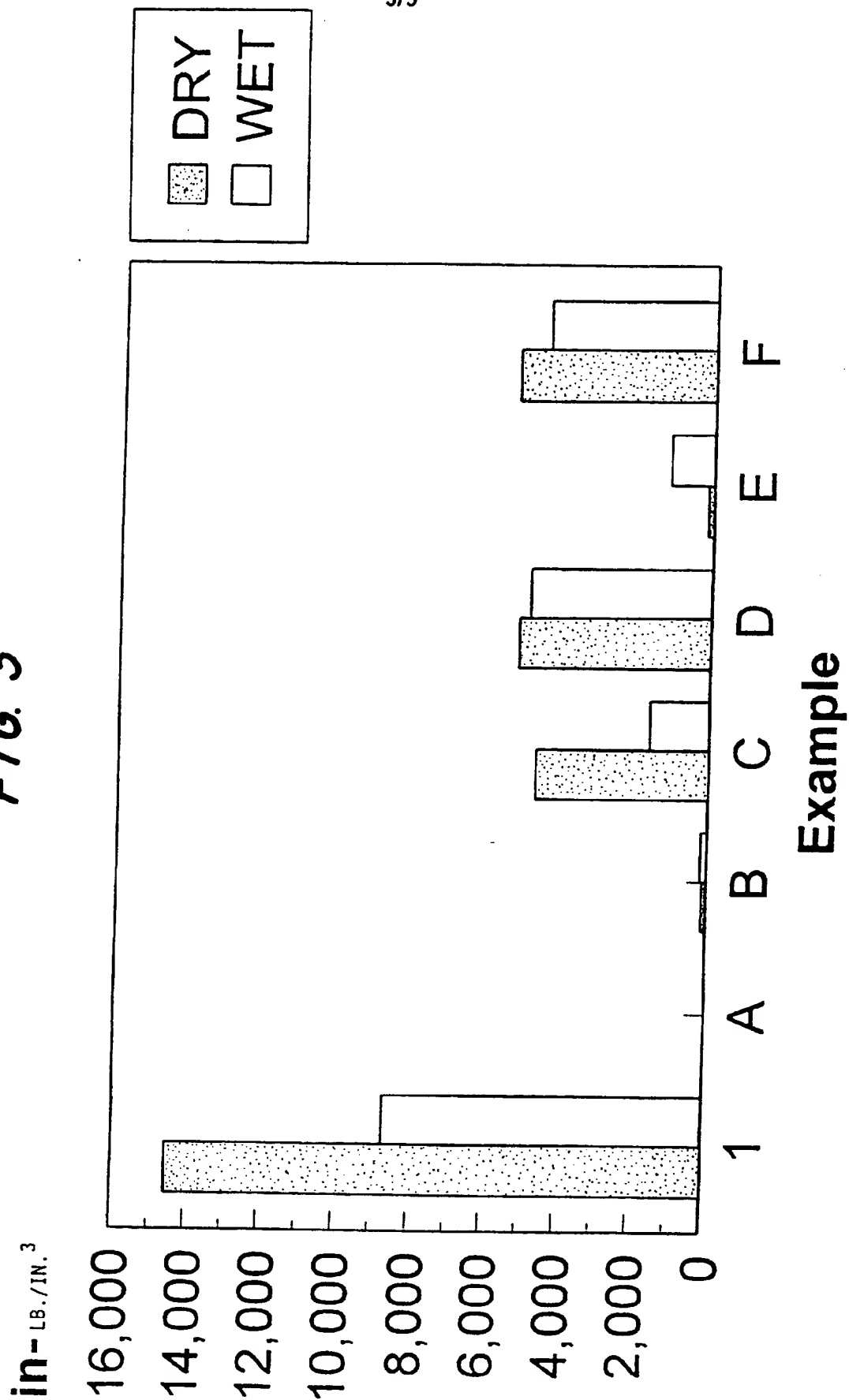
2/3

FIG. 2



3/3

FIG. 3



Example

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/12469

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08G18/48 C08G18/66

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 404 517 (BECTON DICKINSON AND COMPANY) 27 December 1990 see page 2, line 27 - page 4, line 2; claims 1-6; example 6 ---	1
A	EP,A,0 519 314 (B. F. GOODRICH) 23 December 1992 see page 6, line 19 - page 7, line 8; claims 1-3; example 3 ---	1,2
A	GB,A,1 156 784 (ICI) 2 July 1969 see claims 1-4; example 8 ---	1,2
A	WO,A,91 09906 (B.F. GOODRICH) 11 July 1991 see claims; example 3 ---	1,2
A	US,A,4 532 316 (HENN) 30 July 1985 cited in the application ---	
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 March 1995

Date of mailing of the international search report

27. 04. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Bourgonje, A

# INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/US 94/12469

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 901 852 (SHAH) 26 August 1975 cited in the application -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/12469

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0404517	27-12-90	US-A-	5061254	29-10-91
		CA-A-	2017951	22-12-90
		CA-A-	2017952	22-12-90
		JP-A-	3082473	08-04-91
		JP-C-	1822865	10-02-94
		JP-A-	3275068	05-12-91
		JP-B-	5028633	26-04-93
-----				
EP-A-0519314	23-12-92	CA-A-	2071369	21-12-92
		JP-A-	5222289	31-08-93
-----				
GB-A-1156784	02-07-69	NONE		
-----				
WO-A-9109906	11-07-91	EP-A-	0507873	14-10-92
		US-A-	5342889	30-08-94
-----				
US-A-4532316	30-07-85	AT-T-	108469	15-07-94
		AU-B-	555571	02-10-86
		AU-A-	4102185	05-12-85
		CA-A-	1236945	17-05-88
		DE-D-	3587878	18-08-94
		DE-T-	3587878	17-11-94
		EP-A-	0172610	26-02-86
		GB-A, B	2159526	04-12-85
		JP-B-	3054128	19-08-91
		JP-A-	61051020	13-03-86
-----				
US-A-3901852	26-08-75	CA-A-	1067246	27-11-79
		DE-A-	2532040	19-02-76
		FR-A, B	2280663	27-02-76
		GB-A-	1464505	16-02-77
		JP-C-	976766	30-10-79
		JP-A-	51037192	29-03-76
		JP-B-	54010034	01-05-79
		NL-A-	7508970	02-02-76